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(71)Applicant : DAIDO STEEL CO LTD

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(72)Inventor : KOYAMA KEIJI  
 NISHIO TAKAYUKI  
 FURUYA TAKASHI

## (54) QUENCHED THIN BAND FOR BOND MAGNET, PARTICLES FOR BOND MAGNET, BOND MAGNET AND MANUFACTURE THEREOF

## (57)Abstract:

PURPOSE: To provide a manufacturing method of quenched thin band, particles for a bond magnet and a bond magnet in excellent magnetic characteristics.

CONSTITUTION: The mean crystalline particle diameter of the quenched thin band for a bond magnet produced by quenching a molten metal containing specific amount of alloy component is at least  $1\mu\text{m}$  in composition formula of  $\text{RxFc}100-x-y-v\text{ByGev}$ , provided R mainly comprising rare earth element such as Nd to be partly substituted with at least one out of Dy or Pr satisfying the following inequalities of  $9 \leq x \leq 15$   $4 \leq y \leq 10$   $0.1 \leq v \leq 3$ . By the addition of Ge, the magnetic characteristics of the quenched thin band especially the maximum energy product can be improved compared with that whereto Ge is not added. Besides, Ge can be partly substituted with exceeding one or two kinds of alloy component M selected out of Zr, Al, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W.

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CLAIMS

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[Claim(s)]

[Claim 1] The diameter of average crystal grain which quenches the molten metal containing the alloy content of the specified quantity, and is obtained is 1 micrometer or less. As for  $R_xFe_{100-x-y-v}ByGev$ , however R, the empirical formula uses Nd as a principal component. The part is the rare earth component which may be permuted by either [ at least ] Dy or Pr, and they are  $9 \leq x \leq 15$ ,  $4 \leq y \leq 10$ ,  $0.1 \leq v \leq 3$ , and the quenching thin band for bond magnets that comes out and is characterized by a certain thing.

[Claim 2] The diameter of average crystal grain which quenches the molten metal containing the alloy content of the specified quantity, and is obtained is 1 micrometer or less.  $R_xFe_{100-x-y-v}By(GewM1-w)v$ : The empirical formula corrects. It is the rare earth component by which R uses Nd as a principal component, and the part may be permuted by either [ at least ] Dy or Pr. And M It is one sort chosen from from among Zr, aluminum, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W, or two sorts or more, and they are  $9 \leq x \leq 15$ ,  $4 \leq y \leq 10$ ,  $0.05 \leq w \leq 1$ ,  $0.1 \leq v \leq 3$ , and the quenching thin band for bond magnets that comes out and is characterized by a certain thing.

[Claim 3] The diameter of average crystal grain which quenches the molten metal containing the alloy content of the specified quantity, and is obtained is 1 micrometer or less.  $R_xFe_{100-x-y-v}CozByGev$ : The empirical formula corrects. R is the rare earth component by which Nd is used as a principal component and the part may be permuted by either [ at least ] Dy or Pr, and is  $9 \leq x \leq 15$ ,  $4 \leq y \leq 10$ ,  $0 \leq z \leq 30$ ,  $0.1 \leq v \leq 3$ , and a quenching thin band for bond magnets that comes out and is characterized by a certain thing.

[Claim 4] The diameter of average crystal grain which quenches the molten metal containing the alloy content of the specified quantity, and is obtained is 1 micrometer or less.  $R_xFe_{100-x-y-z-v}CozBy(GewM1-w)v$ : The empirical formula corrects. It is the rare

earth component by which R uses Nd as a principal component, and the part may be permuted by either [ at least ] Dy or Pr. And M one sort chosen from among Zr, aluminum, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W, or two sorts or more .. it is ..  $9 \leq x \leq 15$ ,  $4 \leq y \leq 10$ ,  $0 < z \leq 30$ ,  $0.05 \leq w < 1$ ,  $0.1 \leq v \leq 3$ , and the quenching thin band for bond magnets that comes out and is characterized by a certain thing.

[Claim 5] Powder for bond magnets which grinds the quenching thin band for bond magnets according to claim 1 to 4, is obtained, and is characterized by the mean particle diameter being 500 micrometers or less.

[Claim 6] The bond magnet characterized by carrying out resin bond of the powder for bond magnets according to claim 5.

[Claim 7] The manufacture approach of the quenching thin band for bond magnets which is the manufacture approach of the quenching thin band for bond magnets according to claim 1 to 4, and is characterized by including the process which dissolves the alloy content after blending the alloy content of the specified quantity, and the process which carries out the rapid solidification of the dissolved molten metal to the shape of thin band-like one thru/or a flake.

[Claim 8] The manufacture approach of the powder for bond magnets characterized by grinding the quenching thin band for bond magnets obtained by the approach according to claim 7 so that the mean particle diameter may be set to 500 micrometers or less.

[Claim 9] For said grinding front stirrup, said quenching thin band is the manufacture approach of the powder for bond magnets according to claim 8 of heat-treating in a 400-1000-degree C temperature requirement after grinding.

[Claim 10] The manufacture approach of the bond magnet characterized for the powder for bond magnets obtained by the approach according to claim 8 or 9 by pressing or carrying out injection molding after mixing with a resinous principle.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the quenching thin band for bond magnets which uses Nd, Fe, and B as a principal component, the powder for bond magnets, bond magnets, and those manufacture approaches.

#### [0002]

[Description of the Prior Art] Since a Nd-Fe-B system magnet ingredient has the magnetic properties which conflicted, divided and were excellent in the high performance rare earth magnet ingredient, it is widely used for the motor for various electrical machinery and apparatus or automobiles, or the voice coil motor for computers. This Nd-Fe-B system magnet ingredient is divided roughly into three kinds, a sintered magnet, a hot-working magnet, and a bond magnet (resin bond magnet), by that process. Among these, a bond magnet grinds the quenching thin band which carries out the alloy content of the specified quantity by combination / dissolution back, it makes carry out the rapid solidification of the molten metal by the single rolling method etc., and is obtained, makes raw material magnet powder, fabricates the powder with resin binders, such as an epoxy resin or Nylon, and uses it as the magnet of a desired configuration. The above-mentioned magnet powder has the fine crystal grain organization where the Nd<sub>2</sub>Fe<sub>14</sub>B mold tetragonal intermetallic compound phase (henceforth a 2·14·plane 1) which are main hard magnetism phases became below the diameter of a single domain particle, and shows high coercive force in the state of powder. Unlike a sintered magnet and a cold workable magnet, processing after shaping has almost high dimensional accuracy at needlessness, and such a bond magnet is excellent in a configuration degree of freedom, and moreover, since productivity is high, it is especially used for the ring magnet for small motors etc. in large quantities.

#### [0003]

[Problem(s) to be Solved by the Invention] While excelling in the configuration degree of freedom, the easy magnetization direction (the direction of a c-axis of \*\*\*\*\*) of each crystal grain of a 2-14-plane 1 be the so-called isotropic magnet arranged at random within the powder particle, for example, the above-mentioned Nd-Fe-B system bond magnet had a fault with a low maximum energy product compared with the sintered magnet in which anisotropy-izing be possible by the orientation in a field of a magnet fine-particles particle, and 10MGOe extent be a limitation with 6MGOe(s) and a compression-molding magnet in the injection-molding magnet in mass-production level. [0004] By devising the alloy content which permutes Fe component of the quenching thin band for Nd-Fe-B system bond magnets, the technical problem of this invention offers the quenching thin band for bond magnets which was excellent in magnetic properties, especially a maximum energy product, and its manufacture approach, and is to offer [ the powder for bond magnets using the quenching thin band and a bond magnet, and ] those manufacture approaches further.

[0005]

[Means for Solving the Problem and its Function and Effect] In order to solve the above-mentioned problem, the quenching thin band for bond magnets of this invention The diameter of average crystal grain which quenches the molten metal containing the alloy content of the specified quantity, and is obtained is 1 micrometer or less. the rare earth component by which, as for  $R_xFe_{100-x}yv$  ByGev; however R, the empirical formula uses Nd as a principal component, and the part may be permuted by either [ at least ] Dy or Pr -- it is  $9 \leq x \leq 15$ ,  $4 \leq y \leq 10$ , and  $0.1 \leq v \leq 3$  -- it comes out and is characterized by a certain thing.

[0006] By quenching from a molten metal, since the organization where the large  $R_2Fe_{14}B$  mold tetragonal intermetallic-compound phase (henceforth a 2-14-plane 1) became a fine crystal grain with a mean particle diameter of 1 micrometer or less is produced and high coercive force and a high residual magnetic flux density are shown in the condition immediately after quenching, each of saturation magnetic flux density and uniaxial-crystal magnetic anisotropies can use the above-mentioned quenching thin band as a raw material for bond magnets of high performance as it is, if this is ground to the powder of predetermined particle diameter. In addition, if the above-mentioned mean particle diameter exceeds 1 micrometer, since the coercive force of a thin band thru/or the square shape nature of a demagnetization curve will be spoiled and sufficient magnet engine performance will no longer be obtained, the mean particle diameter is made into the thing of the above-mentioned range, and is desirably set to 0.1 micrometers or less still more desirably 0.5 micrometers or less.

[0007] The description of the quenching thin band of this invention is to add germanium within the limits of 0.1 · 3 atom % in the form where a part of Fe is permuted (namely, setting to said empirical formula  $0.1 \leq v \leq 3$ ), and this invention persons find out a good thing by addition of Above germanium compared with that to which the magnetic properties of a quenching thin band, especially a maximum energy product do not add germanium. The reason the addition of germanium is made into an above-mentioned thing is as follows. First, the effectiveness of the maximum energy product improvement by an addition being under 0.1 atom % is no longer acquired fully. On the other hand, if an addition exceeds 3 atom %, the content in the 2·14·plane 1 of germanium which is a nonmagnetic atom will increase, saturation magnetic flux density will fall, and the fall of a maximum energy product will be caused on the contrary. Therefore, the addition of germanium is within the limits, is set [ above-mentioned ] up, and is made into 0.3 to 1.0 atom % desirably [ it is desirable and ] to 0.2 to 1.5 atom %, and a pan. Here, it is possible that crystal grain of a 2·14·plane 1 produced at the time of the rapid solidification of a molten metal is further made detailed by germanium addition as a cause by which the maximum energy product of a quenching thin band goes up, for example etc.

[0008] germanium contained on the above-mentioned quenching thin band can permute the part by one sort or two sorts or more of alloy contents M chosen from among Zr, aluminum, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W. When the sum total content (rate of an atomic ratio) of germanium and an alloy content M is set to 1, the amount of permutations is set up so that the ratio w of germanium content to the sum total content may become less than [ 0.05 or more ] one. That is, it is referred to as  $0.05 \leq w < 1$  when the empirical formula of a quenching thin band is set to  $R_xFe100 \cdot x \cdot y \cdot z \cdot vBy(GewM1 \cdot w)$  v. In addition, the content (atomic %) of germanium and an alloy content M is expressed with  $wxv$  and  $(1-w)xv$ , respectively.

[0009] When germanium is above-mentioned within the limits and is permuted by the alloy content M, the quenching thin band almost equivalent to the case of germanium independent addition which is, carries out and has a maximum energy product beyond it can be obtained. However, if the ratio w of germanium content becomes less than 0.05, since sufficient maximum energy product will no longer be obtained, w is made or more into 0.05. In addition, it is desirably good 0.1 to 0.5, and to set up the ratio w of germanium content within the limits of 0.1·0.3 still more desirably. Moreover, the effectiveness of the improvement in an energy product of the thin band by coaddition with alloying elements M and germanium can be especially acquired notably, when alloying elements M are Zr, Nb, and Mo.

[0010] Moreover, Co can permute a part of Fe component of the above-mentioned quenching thin band by within the limits below 30 atom %. That is, it can be referred to as  $0 < z \leq 30$  when the empirical formula of a quenching thin band is set to  $R_xFe_{100-x} \cdot y \cdot z \cdot vCo_zByGev$  or  $R_xFe_{100-x} \cdot y \cdot z \cdot vCo_zBy(GewM1 \cdot w)$  v. Co is mainly incorporated by the 2·14·plane 1, by making Co contain, while the Curie temperature of a 2·14·plane 1 rises, the temperature coefficient of a residual magnetic flux density is improved, and is above-mentioned presentation within the limits, and can obtain the quenching thin band for bond magnets with which stability and outstanding magnetic properties are secured also in a hot operating environment like the motor for automobiles. Moreover, the chemical stability of a quenching thin band improves by addition of Co, and it is controlled that the bond magnet which used the thin band also under the environment of heat and high humidity is corroded, or magnetic properties fall. However, since the saturation magnetic flux density of a 2·14·plane 1 will fall and it will lead to the fall of a maximum energy product if the content exceeds 30 atom %, it is not desirable. In addition, the content of Co is desirably good 2.5 to 20 atom %, and to set up within the limits of 5 · 10 atom % still more desirably.

[0011] Next, although it is components other than the above, the rare earth component R is a main constituent of the 2·14·plane 1 which bears the magnetic properties which were excellent in the quenching thin band, Nd is made into a subject, and a total content is set as the range of 9 · 15 atom % (namely,  $9 \leq x \leq 15$ ). If the content of the rare earth component R becomes under 9 atom %, the ratio of the alpha-Fe phase which is a soft magnetism phase will increase, and the fall of coercive force will be caused. On the other hand, if 15 atom % is exceeded, the ratio of the nonmagnetic phase which makes a rare earth component a subject will increase, and the fall of saturation magnetic flux density will be caused. Since each of these leads to the fall of a maximum energy product, the content of the rare earth component R is made into the thing of the above-mentioned range, and is desirably good ten to 13 atom %, and to set up within the limits of 11 · 12 atom % still more desirably.

[0012] Moreover, a part of rare earth component R which makes Nd a subject can be permuted by Dy or Pr. By adding Dy, the anisotropy field of the uniaxial magnetic anisotropy of a 2·14·plane 1 is raised, and the coercive force of a quenching thin band can be raised sharply. Thereby, since a fallen part of the coercive force in an elevated temperature is compensated when a magnet is used in the environment where temperature, such as a hard disk drive of a computer and a motor for automobiles, tends to rise, the quenching thin band which is equal to use in a severe temperature environment can be obtained. The addition can be suitably chosen within the limits of

0.1 · pentatomic %. However, since Dy is expensive and it causes a raw material cost rise of a magnet, it is not desirable, except that the saturation magnetic flux density of a 2·14·plane 1 will fall and the fall of a maximum energy product will be caused, if an addition exceeds pentatomic %. In addition, although Tb is still more expensive than Dy, it has effectiveness almost equivalent to Dy, and even if contained by becoming [ a sum total content with Above Dy / 0.1 · pentatomic % ] within the limits, it does not interfere.

[0013] On the other hand, since Pr does not change the value of the saturation magnetic flux density and an anisotropy field so much when Nd in a 2·14·plane 1 is permuted, it is also possible to permute the whole quantity by Pr depending on the considerable amount of Nd component of a quenching thin band and the case, but the separation rare earth of Pr is more expensive than that of Nd, and superfluous combination in the form of the separation rare earth is not desirable in order to cause the rise of raw material cost. However, since raw material cost can be reduced if the separation extract of the Pr is carried out with Nd in the separation purification process of a rare earth raw material, and these are blended in the form of didym (for example, didym metal), since the didym which is the non-dissociating rare earth of Nd and Pr is cheaper than the separation rare earth of Nd and Pr, it is convenient. In this case, the content of Pr in the quenching thin band finally obtained will become settled with Pr content ratio in the didym used.

[0014] In addition, although it is desirable not to contribute to the rise of an energy product, or not to reduce this conversely, and not to contain as much as possible as for each rare earth elements except having described above, even if what the total amount mixes unescapable by within the limits below 1 atom %, for example contains, it does not interfere.

[0015] Next, B is the indispensable constituent of a 2·14·plane 1 like the rare earth component R, and the content is set up within the limits of 4 · 10 atom % (namely,  $4 \leq y \leq 10$ ). If the Nd<sub>2</sub>Fe<sub>17</sub> type phase of soft magnetism will generate, the fall of coercive force will be caused, if the content of B becomes under 4 atom %, and a content exceeds 10 atom %, a nonmagnetic NdFe<sub>4</sub>B<sub>4</sub> type phase will generate and saturation magnetic flux density will fall. Since it is connected with reducing a maximum energy product in any case, let B content be the thing of the above-mentioned range. The content of B is desirably good four to 8 atom %, and to set up within the limits of 5 · 7 atom % still more desirably.

[0016] Fe is contained as the remainders other than the above-mentioned component, and bears the principal part of the big saturation magnetization as an indispensable constituent of a 2·14·plane 1.

[0017] The quenching thin band for bond magnets described above can be ground so

that the mean particle diameter may be set to 500 micrometers or less, and it can be used as the powder for bond magnets. And it can consider as a bond magnet by combining the powder with resin, such as an epoxy resin, phenol resin, and Nylon. Here, since distribution of the magnet [ be / it / 500 micrometers or more ] powder in a bond magnet and resin becomes uneven and the mean particle diameter of the above-mentioned bond magnet powder becomes the cause which produces dispersion in surface magnetic-flux distribution of a bond magnet, let mean particle diameter be the following [ the above ]. On the other hand, since the flow nature of magnet powder will fall, the smooth restoration to the shaping metal mold will become difficult and the fall of productivity will be caused when manufacturing a bond magnet, for example with compression molding if mean particle diameter becomes fine too much, it is set up more than predetermined mean particle diameter. In addition, the mean particle diameter of magnet powder is desirably good to set [ 50-400-micrometer ] up within the limits of 100-300 micrometers still more desirably.

[0018] Hereafter, the manufacture approach of the quenching thin band for bond magnets of this invention, the powder for bond magnets using it, and a bond magnet is explained.

[0019] First, the alloy content of the specified quantity is blended and then the alloy content is dissolved in predetermined ambient atmospheres, such as an inert gas ambient atmosphere or a vacuum ambient atmosphere. The alloy content blended may blend each component independently, or may blend it in the form of hardeners, such as a Nd-Fe alloy and ferroboron, or any are sufficient as it. Moreover, the dissolution can use the well-known dissolution approach, such as for example, the RF induction dissolution and the arc dissolution.

[0020] Next, the quenching thin band of the shape of thin band-like one thru/or a flake is manufactured by carrying out the rapid solidification of the molten metal. Inert gas ambient atmospheres, such as an argon, are used, and the ambient atmosphere of quenching begins the single rolling method as the approach of quenching, and can apply various approaches, such as the congruence rolling method, the Sprat quenching method, a centrifugal quenching method, and the gas atomizing method. It is easy, and the cooling effectiveness of a molten metal is high, and it is [ among these / especially the single rolling method has homogeneous adjustment of the cooling rate by roll peripheral speed and ] suitable for it for mass-producing the quenching thin band of high performance. In this case, it is desirable to make roll peripheral speed desirable in 10-30m/second a second 5-35m /, when obtaining the quenching thin band which has detailed and uniform crystal grain and was excellent in magnetic properties.

[0021] By the well-known grinding approach of using a stamp mill, a feather mill, a disc mill, etc., the obtained quenching thin band is ground so that it may become the above-mentioned mean particle diameter, and let it be the powder for bond magnets. In addition, when the thin band to grind is little, you may grind using a mortar etc.

[0022] Here, the grinding front stirrup can heat-treat after grinding the quenching thin band obtained by said rapid solidification in a 400-1000-degree C temperature requirement. The thin band immediately after quenching may produce the amorphous section for near the contact section for example, with a water-cooled roll etc. into the part to which a cooling rate becomes large especially. This amorphous section is soft magnetism and becomes the cause which causes coercive force, the square shape nature of a demagnetization curve, the fall of an energy product, etc. Then, by performing the above-mentioned heat treatment to a quenching thin band, the above-mentioned amorphous section produced immediately after quenching can be crystallized, and the fall of an energy product etc. can be prevented. Here, when heat treatment temperature is lower than 400 degrees C, crystallization of the above-mentioned amorphous section does not progress enough, and above-mentioned effectiveness is not acquired enough. On the other hand, if heat treatment temperature exceeds 1000 degrees C, crystal grain will grow and make it big and rough, and coercive force thru/or an energy product will fall on the contrary. Therefore, heat treatment temperature is set up within the limits of above-mentioned, and is desirably set up within the limits of 600-700 degrees C still more desirably 500-800 degrees C.

[0023] The powder for bond magnets obtained by the above approach is mixed with a resinous principle, and a bond magnet is manufactured pressing or by carrying out injection molding. the case where it is based on pressing -- the above-mentioned magnet powder -- the thermosetting resin of the shape of powder, such as epoxy resin phenol resin, -- the specified quantity -- for example, it mixes about 1 to 5% of the weight, and this is pressed with about two 5 - 10 t/cm welding pressure with die-press shaping etc. By heating the acquired Plastic solid after shaping to predetermined about temperature, for example, 80-180 degrees C, resin is stiffened and a bond magnet is obtained. In addition, heating for resin hardening may be performed during the above-mentioned pressing. According to this approach, the consistency of the magnet powder in the bond magnet obtained can be made high, and it is suitable for manufacturing the high performance ring magnet for small motors etc.

[0024] the case where it is based on injection molding on the other hand -- first -- thermoplastics, such as Nylon, -- magnet powder -- receiving -- a little more amounts than the case of compression molding -- for example, it adds about 2 to 10% of the

weight, this is kneaded, and the compound for shaping is produced. And the bond magnet of a desired configuration is obtained by carrying out heating softening of this compound, and carrying out injection molding of this using a predetermined making machine. Although it is based on compression molding since the bond magnet obtained by this approach has a little low magnet powder consistency, there is an advantage which can manufacture the magnet of a various and complicated configuration easily, and attached components, such as a motor spindle, can also really be fabricated with the above-mentioned compound.

[0025] In addition, various surface treatment, such as electropainting, dip coating, spray painting, and nickel plating, can be performed to the bond magnet obtained by the above approach.

[0026]

[Example]

(Example 1) The ingot which has the various presentations shown in Table 1 was produced by the arc dissolution, the RF induction dissolution of this ingot was carried out in the quartz crucible which has a nozzle in a point in an argon ambient atmosphere, predetermined argon gas pressure was impressed to this, and the quenching thin band was obtained by injecting a molten metal on the copper roll (single roll) which gave chrome plating from the above-mentioned nozzle. In addition, peripheral speed of a roll was carried out in 20m/second. Next, the thin band was ground so that particle diameter might be set to 300 micrometers or less with a mortar, further, in the argon ambient atmosphere, it heat-treated in the 600-800-degree C temperature requirement, and the bond magnet powder of each presentation was obtained. Mixed non-hardened epoxy resin powder, and heated after compression molding and a Plastic solid to these magnet powder by the pressure of 9 t/cm<sup>2</sup>, it was made to harden resin, and the bond magnet was obtained. The magnetization curve of the obtained bond magnet was measured at the room temperature with the B-H marker, and it asked for the maximum energy product ((BH) max). A result is shown in Table 1.

[0027]

[Table 1]

NO.	合金組成 (原子百分率)	(BH)max[MGOe]
1	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Ge}_{0.2}$	10.5
2	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Ge}_{0.5}$	10.7
3	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Ge}_{1.5}$	10.6
4	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Ge}_{3.0}$	9.5
5	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Zr}_{0.45}\text{Ge}_{0.05}$	11.5
6	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Zr}_{0.4}\text{Ge}_{0.1}$	11.3
7	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Zr}_{0.25}\text{Ge}_{0.25}$	11.0
8 *	$\text{Nd}_{12}\text{Fe}_{81}\text{B}_{6.5}\text{Zr}_{0.5}$	9.3
9 *	$\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$	7.6

\*比較例

[0028] Each bond magnet (No.1-4) which added germanium is understood that a maximum energy product is large compared with what is not added (No. 8, 9, the example of a comparison). Moreover, (sample numbers 5-7) and a maximum energy product improved further by permuting some germanium by Zr.

[0029] (Example 2) The ingot which has the various presentations shown in Table 2 was created, the bond magnet was produced by the same approach as an example 1, and the maximum energy product was measured. A result is shown in Table 2. The bond magnet (No.10-19) which carried out compound addition of the various alloy contents of aluminum, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W with germanium is understood that a maximum energy product is high compared with what added the above-mentioned alloy

content independently (No.20-29, example of a comparison).

[0030]

[Table 2]

NO.	合金組成 (原子百分率)	(BH)max[MGOe]
10	$Nd_{12}Fe_{81}B_{6.5}Al_{0.45}Ge_{0.05}$	11.1
11	$Nd_{12}Fe_{81}B_{6.5}Si_{0.45}Ge_{0.05}$	10.6
12	$Nd_{12}Fe_{81}B_{6.5}Ti_{0.45}Ge_{0.05}$	10.9
13	$Nd_{12}Fe_{81}B_{6.5}V_{0.45}Ge_{0.05}$	10.5
14	$Nd_{12}Fe_{81}B_{6.5}Ga_{0.45}Ge_{0.05}$	11.2
15	$Nd_{12}Fe_{81}B_{6.5}Nb_{0.45}Ge_{0.05}$	11.3
16	$Nd_{12}Fe_{81}B_{6.5}Mo_{0.45}Ge_{0.05}$	11.3
17	$Nd_{12}Fe_{81}B_{6.5}Hf_{0.45}Ge_{0.05}$	10.9
18	$Nd_{12}Fe_{81}B_{6.5}Ta_{0.45}Ge_{0.05}$	11.4
19	$Nd_{12}Fe_{81}B_{6.5}W_{0.45}Ge_{0.05}$	11.2
20*	$Nd_{12}Fe_{81}B_{6.5}Al_{0.5}$	8.4
21*	$Nd_{12}Fe_{81}B_{6.5}Si_{0.5}$	8.3
22*	$Nd_{12}Fe_{81}B_{6.5}Ti_{0.5}$	8.6
23*	$Nd_{12}Fe_{81}B_{6.5}V_{0.5}$	8.0
24*	$Nd_{12}Fe_{81}B_{6.5}Ga_{0.5}$	7.9
25*	$Nd_{12}Fe_{81}B_{6.5}Nb_{0.5}$	8.5
26*	$Nd_{12}Fe_{81}B_{6.5}Mo_{0.5}$	7.9
27*	$Nd_{12}Fe_{81}B_{6.5}Hf_{0.5}$	8.1
28*	$Nd_{12}Fe_{81}B_{6.5}Ta_{0.5}$	8.2
29*	$Nd_{12}Fe_{81}B_{6.5}W_{0.5}$	8.1

\*比較例

[0031] (Example 3) The ingot which has the various presentations shown in Table 3 was created, the bond magnet was produced by the same approach as an example 1, and the maximum energy product was measured. A result is shown in Table 3. For Co ten atoms % and germanium 0.5 atom % content The bond magnet to carry out (No.30), About this bond magnet, and the bond magnet (No.31-41) which carried out compound addition of the various alloy contents of Zr, aluminum, Si, Ti, V, Ga, Nb, Mo, Hf, Ta, and W with germanium Compared with the thing (No.53, example of a comparison) containing neither the thing (No.42-52, example of a comparison) which added only the

above-mentioned alloy content, without adding germanium nor the above-mentioned alloy content nor germanium, it turns out that a maximum energy product is high.

[0032]

[Table 3]

NO.	合金組成 (原子百分率)	(BH)max[MGOe]
30	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ge}_{0.5}$	11.3
31	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Zr}_{0.45}\text{Ge}_{0.05}$	12.0
32	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Al}_{0.45}\text{Ge}_{0.05}$	11.5
33	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Si}_{0.45}\text{Ge}_{0.05}$	11.4
34	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ti}_{0.45}\text{Ge}_{0.05}$	11.6
35	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{V}_{0.45}\text{Ge}_{0.05}$	11.2
36	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ga}_{0.45}\text{Ge}_{0.05}$	11.4
37	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Nb}_{0.45}\text{Ge}_{0.05}$	11.9
38	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Mo}_{0.45}\text{Ge}_{0.05}$	11.8
39	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Hf}_{0.45}\text{Ge}_{0.05}$	11.5
40	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ta}_{0.45}\text{Ge}_{0.05}$	11.2
41	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{W}_{0.45}\text{Ge}_{0.05}$	11.3
42*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Zr}_{0.5}$	9.4
43*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Al}_{0.5}$	9.3
44*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Si}_{0.5}$	9.3
45*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ti}_{0.5}$	9.2
46*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{V}_{0.5}$	9.0
47*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ga}_{0.5}$	8.8
48*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Nb}_{0.5}$	9.1
49*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Mo}_{0.5}$	9.3
50*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Hf}_{0.5}$	9.0
51*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{Ta}_{0.5}$	9.4
52*	$\text{Nd}_{12}\text{Fe}_{71}\text{Co}_{10}\text{B}_{6.5}\text{W}_{0.5}$	8.7
53*	$\text{Nd}_{12}\text{Fe}_{72}\text{Co}_{10}\text{B}_6$	8.3

\*比較例

[Translation done.]

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(71)出願人 000003713  
大同特殊鋼株式会社  
愛知県名古屋市中区錦一丁目11番18号  
(72)発明者 小山 恵史  
愛知県東海市加木屋町南鹿特18番地  
(72)発明者 西尾 孝幸  
愛知県春日井市岩成台六丁目2番地ノ3  
岩成台団地14-204  
(72)発明者 古谷 崑司  
愛知県知多市梅が丘2-108  
(74)代理人 弁理士 菅原 正倫

(54)【発明の名称】 ポンド磁石用急冷薄帯、ポンド磁石用粉末、ポンド磁石及びそれらの製造方法

(57)【要約】

【目的】 磁気特性の優れたポンド磁石用急冷薄帯、ポンド磁石用粉末、ポンド磁石及びそれらの製造方法を提供する。

【構成】 本発明のポンド磁石用急冷薄帯は、所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が  $1 \mu m$  以下であり、その組成式が、 $R_x F e_1 - 00-x-y-v B y G e_v$  : ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0.1 \leq v \leq 3$ 、とされる。Geの添加により、急冷薄帯の磁気特性、特に最大エネルギー積がGeを添加しないものに比べて良好となる。Geは、その一部をZr、Al、Si、Ti、V、Ga、Nb、Mo、Hf、Ta、Wのうちから選択される1種又は2種以上の合金成分Mで置換することができる。

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## 【特許請求の範囲】

【請求項1】 所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が $1\text{ }\mu\text{m}$ 以下であり、その組成式が、

$R_xFe_{100-x-y-v}ByGe_v$  :

ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0.1 \leq v \leq 3$ 、

であることを特徴とするボンド磁石用急冷薄帯。

【請求項2】 所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が $1\text{ }\mu\text{m}$ 以下であり、その組成式が、

$R_xFe_{100-x-y-v}By(Ge_wM_{1-w})_v$  :

ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、かつMは、Zr、Al、Si、Ti、V、Ga、Nb、Mo、Hf、Ta、Wのうちから選択される1種又は2種以上であって、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0.05 \leq w < 1$ 、 $0.1 \leq v \leq 3$ 、

であることを特徴とするボンド磁石用急冷薄帯。

【請求項3】 所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が $1\text{ }\mu\text{m}$ 以下であり、その組成式が、

$R_xFe_{100-x-y-v}Co_zByGe_v$  :

ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0 < z \leq 30$ 、 $0.1 \leq v \leq 3$ 、

であることを特徴とするボンド磁石用急冷薄帯。

【請求項4】 所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が $1\text{ }\mu\text{m}$ 以下であり、その組成式が、

$R_xFe_{100-x-y-z-v}Co_zBy(Ge_wM_{1-w})_v$  :

ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、かつMは、Zr、Al、Si、Ti、V、Ga、Nb、Mo、Hf、Ta、Wのうちから選択される1種又は2種以上であって、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0 < z \leq 30$ 、 $0.05 \leq w < 1$ 、 $0.1 \leq v \leq 3$ 、

であることを特徴とするボンド磁石用急冷薄帯。

【請求項5】 請求項1ないし4のいずれかに記載のボンド磁石用急冷薄帯を粉碎して得られ、その平均粒子径が $500\text{ }\mu\text{m}$ 以下であることを特徴とするボンド磁石用粉末。

【請求項6】 請求項5記載のボンド磁石用粉末が樹脂結合されたことを特徴とするボンド磁石。

【請求項7】 請求項1ないし4のいずれかに記載のボンド磁石用急冷薄帯の製造方法であって、

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所定量の合金成分を配合後、その合金成分を溶解する工程と、

その溶解された溶湯を薄帯状ないしフレーク状に急冷凝固させる工程と、

を含むことを特徴とするボンド磁石用急冷薄帯の製造方法。

【請求項8】 請求項7記載の方法により得られるボンド磁石用急冷薄帯を、その平均粒子径が $500\text{ }\mu\text{m}$ 以下となるように粉碎することを特徴とするボンド磁石用粉末の製造方法。

【請求項9】 前記急冷薄帯が、前記粉碎前又は粉碎後に $400\text{ }-\text{ }1000\text{ }^{\circ}\text{C}$ の温度範囲において熱処理される請求項8記載のボンド磁石用粉末の製造方法。

【請求項10】 請求項8又は9記載の方法により得られるボンド磁石用粉末を樹脂成分と混合後、加圧成形又は射出成形することを特徴とするボンド磁石の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、Nd、Fe及びBを主成分とするボンド磁石用急冷薄帯、ボンド磁石用粉末、ボンド磁石及びそれらの製造方法に関する。

## 【0002】

【従来の技術】 Nd-Fe-B系磁石材料は、高性能希土類磁石材料の中でもとりわけ優れた磁気特性を有することから、各種電気機器や自動車用のモータ、あるいはコンピュータ用のポイスコイルモータ等に広く使用されている。このNd-Fe-B系磁石材料は、その製法により、焼結磁石、熱間加工磁石及びボンド磁石（樹脂結合磁石）の3種類に大別される。このうちボンド磁石は、所定量の合金成分を配合・溶解後、溶湯を単ロール法等により急冷凝固させて得られる急冷薄帯を粉碎して原料磁石粉末を作り、その粉末をエポキシ樹脂、あるいはナイロン樹脂等の樹脂バインダとともに成形して所望の形状の磁石とするものである。上記磁石粉末は、主要な硬磁性相であるNd<sub>2</sub>Fe<sub>14</sub>B型正方晶金属間化合物相（以下2-14-1相という）が单磁区粒子径以下となつた微細結晶粒組織を有し、粉末の状態で高い保磁力を示す。このようなボンド磁石は、焼結磁石及び圧延磁石と異なり成形後の加工がほとんど不要で寸法精度が高く、形状自由度に優れ、しかも生産性が高いことから、特に小型モーター用のリング磁石などに大量に使用されている。

## 【0003】

【発明が解決しようとする課題】 上記Nd-Fe-B系ボンド磁石は形状自由度に優れている反面、粉末粒子内で2-14-1相の各結晶粒の容易磁化方向（正方晶のc軸方向）がランダムに配列したいわゆる等方性磁石であり、例えば磁石粉体粒子の磁界中配向により異方性化が可能な焼結磁石等に比べて最大エネルギー積が低い欠

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点があり、量産レベルにおいて射出成形磁石で6MGOe、圧縮成形磁石で10MGOe程度が限界であった。

【0004】本発明の課題は、Nd-Fe-B系ボンド磁石用急冷薄帯のFe成分を置換する合金成分を工夫することにより、磁気特性、特に最大エネルギー積の優れたボンド磁石用急冷薄帯及びその製造方法を提供し、その急冷薄帯を用いたボンド磁石用粉末ならびにボンド磁石、さらにはそれらの製造方法を提供することにある。

【0005】

【課題を解決するための手段、作用及び効果】上記した問題を解決するために、本発明のボンド磁石用急冷薄帯は、所定量の合金成分を含む溶湯を急冷して得られるその平均結晶粒径が1μm以下であり、その組成式が、 $R_xFe_{100-x-y-v}ByGe_v$ ：ただし、RはNdを主成分とし、その一部がDyないしPrの少なくとも一方によって置換される場合がある希土類成分であり、 $9 \leq x \leq 15$ 、 $4 \leq y \leq 10$ 、 $0.1 \leq v \leq 3$ 、であることを特徴とする。

【0006】上記急冷薄帯は、溶湯からの急冷により、飽和磁束密度及び一軸結晶磁気異方性がいずれも大きい $R_2Fe_{14}B$ 型正方晶金属間化合物相（以下2-14-1相という）が平均粒径1μm以下の微細結晶粒となつた組織を生じ、急冷直後の状態で高い保磁力と残留磁束密度を示すので、これを所定の粒子径の粉末に粉碎すればそのまま高性能のボンド磁石用原料として使用できる。なお、上記平均粒径が1μmを超えると、薄帯の保磁力ないし減磁曲線の角形性が損なわれて充分な磁石性能が得られなくなるので、その平均粒径は上記範囲のものとされ、望ましくは0.5μm以下、さらに望ましくは0.1μm以下とされる。

【0007】本発明の急冷薄帯の特徴は、Geが、Feの一部を置換する形で0.1～3原子%の範囲内で添加されていることにあり（すなわち前記組成式において $0.1 \leq v \leq 3$ ）、本発明者らは、上記Geの添加により、急冷薄帯の磁気特性、特に最大エネルギー積がGeを添加しないものに比べて良好であることを見い出したものである。Geの添加量が上述のものとされる理由は下記の通りである。まず、添加量が0.1原子%未満であると、最大エネルギー積改善の効果が充分に得られなくなる。一方、添加量が3原子%を超えると、非磁性原子であるGeの2-14-1相中の含有量が増大し、飽和磁束密度が低下して、却って最大エネルギー積の低下を招く。従って、Geの添加量は上記範囲内で設定され、望ましくは0.2～1.5原子%、さらに望ましくは0.3～1.0原子%とされる。ここで、急冷薄帯の最大エネルギー積が上昇する原因としては、例えば、溶湯の急冷凝固時に生ずる2-14-1相の結晶粒がGe添加により、さらに微細化されること等が考えられる。

【0008】上記急冷薄帯に含有されるGeは、その一部をZr、Al、Si、Ti、V、Ga、Nb、Mo、

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Hf、Ta、Wのうちから選択される1種又は2種以上の合金成分Mで置換することができる。その置換量は、Geと合金成分Mとの合計含有量（原子比率）を1とした場合、その合計含有量に対するGe含有量の比率wが、0.05以上1未満となるように設定される。すなわち、急冷薄帯の組成式を $R_xFe_{100-x-y-z-v}By(Ge_wM_{1-w})_v$ とした場合に、 $0.05 \leq w < 1$ とされる。なお、Ge及び合金成分Mの含有量（原子%）は、それぞれ $w \times v$ 及び $(1-w) \times v$ で表される。

【0009】Geが合金成分Mにより上記範囲内で置換されることにより、Ge単独添加の場合とほぼ同等ないしそれ以上の最大エネルギー積を有する急冷薄帯を得ることができる。ただし、Ge含有量の比率wが0.05未満となると、充分な最大エネルギー積が得られなくなるので、wは0.05以上とされる。なお、Ge含有量の比率wは、望ましくは0.1～0.5、さらに望ましくは0.1～0.3の範囲内で設定するのがよい。また、添加元素MとGeとの共添加による薄帯のエネルギー積向上の効果は、添加元素MがZr、Nb、Moの場合に特に顕著に得ることができる。

【0010】また、上記急冷薄帯のFe成分の一部を、30原子%以下の範囲内でCoにより置換することができる。すなわち、急冷薄帯の組成式を $R_xFe_{100-x-y-z-v}Co_zBy(Ge_wM_{1-w})_v$ あるいは $R_xFe_{100-x-y-z-v}Co_zBy(Ge_wM_{1-w})_v$ とした場合に、 $0 < z \leq 30$ とすることができます。Coは主に2-14-1相に取り込まれ、上記組成範囲内でCoを含有させることにより、2-14-1相のキュリー温度が上昇するとともに残留磁束密度の温度係数が改善され、自動車用モータのような高温の使用環境においても、安定かつ優れた磁気特性が確保されるボンド磁石用急冷薄帯を得ることができる。また、Coの添加により急冷薄帯の化学的安定性が向上し、高温多湿の環境下でも、その薄帯を用いたボンド磁石が腐食されたり磁気特性が低下したりすることが抑制される。しかしながら、その含有量が30原子%を超えると2-14-1相の飽和磁束密度が低下し、最大エネルギー積の低下につながるので好ましくない。なお、Coの含有量は、望ましくは2.5～20原子%、さらに望ましくは5～10原子%の範囲内で設定するのがよい。

【0011】次に、上記以外の成分であるが、希土類成分Rは急冷薄帯の優れた磁気特性を担う2-14-1相の主要構成成分であって、Ndを主体とし、合計の含有量が9～15原子%の範囲に設定される（すなわち $9 \leq x \leq 15$ ）。希土類成分Rの含有量が9原子%未満になると、軟磁性相であるα-Fe相の比率が増大し、保磁力の低下を招く。一方、15原子%を超えると希土類成分を主体とする非磁性相の比率が増大し、飽和磁束密度の低下を招く。これらはいずれも最大エネルギー積の低下につながるので、希土類成分Rの含有量は上記範囲の

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ものとされ、望ましくは10～13原子%、さらに望ましくは11～12原子%の範囲内で設定するのがよい。

【0012】また、Ndを主体とする希土類成分Rの一部をDy又はPrで置換することができる。Dyを添加することにより、2-14-1相の一軸磁気異方性の異方性磁界が高められ、急冷薄帯の保磁力を大幅に向上させることができる。これにより、例えばコンピュータのハードディスクドライブや自動車用のモータなど、温度が上昇しやすい環境で磁石が使用される場合、高温での保磁力の低下分が補われるので、厳しい温度環境での使用に耐える急冷薄帯を得ることができる。その添加量は、例えば0.1～5原子%の範囲内で適宜選択できる。ただし、添加量が5原子%を超えると2-14-1相の飽和磁束密度が低下し、最大エネルギー積の低下を招くほか、Dyは高価であるため磁石の原料コスト上昇を招くので好ましくない。なお、TbはDyよりもさらに高価であるが、Dyとほぼ同等の効果を有しており、上記Dyとの合計含有量が0.1～5原子%となるの範囲内で含有されていても差しつかえない。

【0013】一方、Prは2-14-1相中のNdを置換した場合に、その飽和磁束密度及び異方性磁界の値をそれほど変化させないため、急冷薄帯のNd成分の相当量、場合によってはその全量をPrで置換することも可能であるが、Prの分離希土はNdのそれよりも高価であり、その分離希土の形での過剰な配合は、原料コストの上昇を招くため好ましくない。しかしながら、Prは希土類原料の分離精製工程においてNdとともに分離抽出され、NdとPrの非分離希土であるジジムはNd及びPrの分離希土よりも安価であるので、これらをジジム（例えばジジムメタル）の形で配合すれば原料コストを低減することができるので好都合である。この場合、最終的に得られる急冷薄帯中のPrの含有量は、使用されるジジム中のPr含有比率により定まることとなる。

【0014】なお、上記した以外の希土類元素は、いずれもエネルギー積の上昇に寄与しないか逆にこれを低下させるものであり、できるだけ含有されないことが望ましいが、例えばその総量が1原子%以下の範囲内で不可避免に混入するものは含有されていても差しつかえない。

【0015】次に、Bは、希土類成分Rと同様に2-14-1相の必須構成成分であり、その含有量は4～10原子%の範囲内（すなわち $4 \leq y \leq 10$ ）で設定される。Bの含有量が4原子%未満となると、軟磁性のNd<sub>2</sub>Fe<sub>17</sub>型相が生成して保磁力の低下を招き、含有量が10原子%を超えると非磁性のNd<sub>2</sub>Fe<sub>4</sub>B<sub>4</sub>型相が生成して飽和磁束密度が低下する。いずれの場合も、最大エネルギー積を低下させることにつながるので、B含有量は上記範囲のものとされる。Bの含有量は、望ましくは4～8原子%、さらに望ましくは5～7原子%の範囲内で設定するのがよい。

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【0016】Feは、上記成分以外の残部として含有され、2-14-1相の必須構成成分として、その大きな飽和磁化の主要部を担うものである。

【0017】以上述べたボンド磁石用急冷薄帯は、その平均粒子径が500μm以下となるように粉碎してボンド磁石用粉末とすることができます。そして、その粉末をエポキシ樹脂、フェノール樹脂、ナイロン樹脂等の樹脂により結合することにより、ボンド磁石とすることができます。ここで、上記ボンド磁石粉末の平均粒子径が50.10μm以上であると、ボンド磁石内における磁石粉末及び樹脂の分布が不均一となり、ボンド磁石の表面磁束分布のばらつきを生ずる原因となるので、平均粒子径は上記以下のものとされる。一方、平均粒子径が細かくなりすぎると、例えば圧縮成形によりボンド磁石を製造する場合、磁石粉末の流れ性が低下し、その成形金型へのスムーズな充填が困難になり生産性の低下を引き起こすので、所定の平均粒子径以上に設定される。なお、磁石粉末の平均粒子径は、望ましくは50～400μm、さらに望ましくは100～300μmの範囲内で設定するの20がよい。

【0018】以下、本発明のボンド磁石用急冷薄帯、それを用いたボンド磁石用粉末及びボンド磁石の製造方法について説明する。

【0019】まず、所定量の合金成分を配合し、次に不活性ガス雰囲気あるいは真空雰囲気等、所定の雰囲気中でその合金成分を溶解する。配合される合金成分は、それぞれの成分を単独で配合しても、Nd-Fe合金やフェロボロン等の母合金の形で配合してもいずれでもよい。また、溶解は、例えば高周波誘導溶解、アーク溶解等公知の溶解方法を用いることができる。

【0020】次に、その浴湯を急冷凝固させることにより、薄帯状ないしフレーク状の急冷薄帯が製造される。急冷の雰囲気は、例えばアルゴン等の不活性ガス雰囲気が用いられ、急冷の方法としては、単ロール法を始め、双ロール法、スプラットクエンチ法、遠心急冷法、ガスアトマイズ法等、各種方法が適用できる。これらのうち、特に単ロール法は、浴湯の冷却効率が高く、またロール周速による冷却速度の調整が容易で、均質で高性能の急冷薄帯を大量生産するのに好適である。この場合、40ロール周速を5～35m/秒、望ましくは10～30m/秒とすることが、微細で均一な結晶粒を有し、磁気特性に優れた急冷薄帯を得る上で望ましい。

【0021】得られた急冷薄帯は、スタンプミル、フェザーミル、ディスクミル等を用いる公知の粉碎方法により、前述の平均粒子径となるように粉碎され、ボンド磁石用粉末とされる。なお、粉碎する薄帯が少量の場合は、乳鉢等を用いて粉碎してもよい。

【0022】ここで、前記急冷凝固により得られる急冷薄帯は、その粉碎前又は粉碎後に400～1000℃の50温度範囲において熱処理することができる。急冷直後の

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薄帯は、例えば水冷ロールとの接触部付近等、冷却速度の特に大きくなる部分に非晶質部を生じる場合がある。この非晶質部は軟磁性であり、保磁力、減磁曲線の角型性、エネルギー積の低下等を引き起こす原因となる。そこで、急冷薄帯に対し上記熱処理を行うことにより、急冷直後に生じていた上記非晶質部を結晶化することができ、エネルギー積の低下等を防止することができる。ここで、熱処理温度が400°Cより低い場合は、上記非晶質部の結晶化が充分進まず、上述の効果が充分得られない。一方、熱処理温度が1000°Cを超えると、結晶粒が成長して粗大化し、保磁力ないしエネルギー積は却つて低下する。従って、熱処理温度は上述の範囲内で設定され、望ましくは500~800°C、さらに望ましくは600~700°Cの範囲内で設定される。

【0023】以上的方法により得られるボンド磁石用粉末を樹脂成分と混合し、加圧成形又は射出成形することによりボンド磁石が製造される。加圧成形による場合は、上記磁石粉末に、エポキシ樹脂フェノール樹脂等の粉末状の熱硬化性樹脂を所定量、例えば1~5重量%程度混合し、これを金型プレス成形等により、例えば5~10t/cm<sup>2</sup>程度の加圧力で圧縮成形する。成形後、得られた成形体を所定温度、例えば80~180°C程度に加熱することにより樹脂を硬化させ、ボンド磁石を得る。なお、樹脂硬化のための加熱は、上記加圧成形中に行ってもよい。この方法によれば、得られるボンド磁石中の磁石粉末の密度を高くでき、小型モータ用の高性能リング磁石等を製造するのに適している。

【0024】一方、射出成形による場合は、まず、ナイロン樹脂等の熱可塑性樹脂を磁石粉末に対し、圧縮成形の場合よりやや多い量、例えば2~10重量%程度添加し、これを混練して成形用のコンパウンドを作製する。\*

\*そして、このコンパウンドを加熱軟化させ、所定の成形機を用いてこれを射出成形することにより、所望の形状のボンド磁石を得るものである。この方法により得られるボンド磁石は、磁石粉末密度がやや低いため、性能は圧縮成形によるものに及ばないが、多様で複雑な形状の磁石を容易に製造できる利点があり、モータスピンドル等の付属部品を上記コンパウンドとともに一体成形することもできる。

【0025】なお、以上的方法により得られたボンド磁石に、電着塗装、浸漬塗装、スプレー塗装、ニッケルメッキ等の各種表面処理を施すことができる。

【0026】

【実施例】

(実施例1) 表1に示した各種組成を有するインゴットをアーク溶解により作製し、このインゴットをアルゴン雰囲気中で、先端部にノズルを有する石英るつぼ中で高周波誘導溶解し、これに所定のアルゴンガス圧を印加して、溶湯を上記ノズルからクロムメッキを施した銅ロール(単ロール)に射出することにより急冷薄帯を得た。

なお、ロールの周速は20m/秒とした。次に、薄帯を乳鉢により粒子径が300μm以下となるように粉碎し、さらにアルゴン雰囲気中で、600~800°Cの温度範囲で熱処理して各組成のボンド磁石粉末を得た。これら磁石粉末に、未硬化のエポキシ樹脂粉末を混合し、9t/cm<sup>2</sup>の圧力で圧縮成形の後、成形体を加熱して樹脂を硬化させ、ボンド磁石を得た。得られたボンド磁石の磁化曲線をB-Hトレーサにより室温で測定し、最大エネルギー積((B·H)max)を求めた。結果を表1に示す。

【0027】

【表1】

NO.	合金組成(原子百分率)	(B·H)max[MGOe]
1	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ge <sub>0.2</sub>	10.5
2	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ge <sub>0.3</sub>	10.7
3	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ge <sub>1.5</sub>	10.6
4	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ge <sub>3.0</sub>	9.5
5	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Zr <sub>0.05</sub> Ge <sub>0.05</sub>	11.5
6	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Zr <sub>0.4</sub> Ge <sub>0.1</sub>	11.3
7	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Zr <sub>0.25</sub> Ge <sub>0.25</sub>	11.0
8*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Zr <sub>0.5</sub>	9.3
9*	Nd <sub>12</sub> Fe <sub>82</sub> B <sub>6</sub>	7.6

\*比較例

【0028】Geを添加したボンド磁石(No.1~4)はいずれも、添加しないもの(No.8, 9、比較例)に比べて最大エネルギー積が大きいことがわかる。また、Geの一部をZrで置換することにより(試料番

号5~7)、最大エネルギー積はさらに向上した。

【0029】(実施例2)表2に示した各種組成を有するインゴットを作成し、実施例1と同様の方法によりボンド磁石を作製し、その最大エネルギー積を測定した。

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結果を表2に示す。Al、Si、Ti、V、Ga、Nb、Mo、Hf、Ta、Wの各種合金成分をGeとともに複合添加したボンド磁石（No. 10～19）は、上記合金成分を単独で添加したもの（No. 20～29、\*）

\* 比較例）に比べて最大エネルギー積が高いことがわかる。

【0030】

【表2】

NO.	合金組成（原子百分率）	(BH)max[MGoe]
10	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Al <sub>0.45</sub> Ge <sub>0.05</sub>	11.1
11	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Si <sub>0.45</sub> Ge <sub>0.05</sub>	10.6
12	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ti <sub>0.45</sub> Ge <sub>0.05</sub>	10.9
13	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> V <sub>0.45</sub> Ge <sub>0.05</sub>	10.5
14	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ga <sub>0.45</sub> Ge <sub>0.05</sub>	11.2
15	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Nb <sub>0.45</sub> Ge <sub>0.05</sub>	11.3
16	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Mo <sub>0.45</sub> Ge <sub>0.05</sub>	11.3
17	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Hf <sub>0.45</sub> Ge <sub>0.05</sub>	10.9
18	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ta <sub>0.45</sub> Ge <sub>0.05</sub>	11.4
19	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> W <sub>0.45</sub> Ge <sub>0.05</sub>	11.2
20*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Al <sub>0.5</sub>	8.4
21*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Si <sub>0.5</sub>	8.3
22*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ti <sub>0.5</sub>	8.6
23*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> V <sub>0.5</sub>	8.0
24*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ga <sub>0.5</sub>	7.9
25*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Nb <sub>0.5</sub>	8.5
26*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Mo <sub>0.5</sub>	7.9
27*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Hf <sub>0.5</sub>	8.1
28*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> Ta <sub>0.5</sub>	8.2
29*	Nd <sub>12</sub> Fe <sub>81</sub> B <sub>6.5</sub> W <sub>0.5</sub>	8.1

\*比較例

【0031】（実施例3）表3に示した各種組成を有するインゴットを作成し、実施例1と同様の方法によりボンド磁石を作製し、その最大エネルギー積を測定した。結果を表3に示す。Coを10原子%ならびにGeを0.5原子%含有するボンド磁石（No. 30）、及びこのボンド磁石について、Zr、Al、Si、Ti、V、Ga、Nb、Mo、Hf、Ta、Wの各種合金成分

をGeとともに複合添加したボンド磁石（No. 31～41）は、Geを添加せずに上記合金成分のみを添加したもの（No. 42～52、比較例）、及び上記合金成分及びGeのいずれも含有しないもの（No. 53、比較例）に比べて最大エネルギー積が高いことがわかる。

【0032】

【表3】

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NO.	合金組成 (原子百分率)	(BH)max[MGOe]
30	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ge_{0.5}$	11.3
31	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Zr_{0.45}Ge_{0.05}$	12.0
32	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Al_{0.45}Ge_{0.05}$	11.5
33	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Si_{0.45}Ge_{0.05}$	11.4
34	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ti_{0.45}Ge_{0.05}$	11.6
35	$Nd_{12}Fe_{71}Co_{10}B_{6.5}V_{0.45}Ge_{0.05}$	11.2
36	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ga_{0.45}Ge_{0.05}$	11.4
37	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Nb_{0.45}Ge_{0.05}$	11.9
38	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Mo_{0.45}Ge_{0.05}$	11.8
39	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Hf_{0.45}Ge_{0.05}$	11.5
40	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ta_{0.45}Ge_{0.05}$	11.2
41	$Nd_{12}Fe_{71}Co_{10}B_{6.5}W_{0.45}Ge_{0.05}$	11.3
42*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Zr_{0.5}$	9.4
43*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Al_{0.5}$	9.3
44*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Si_{0.5}$	9.3
45*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ti_{0.5}$	9.2
46*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}V_{0.5}$	9.0
47*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ga_{0.5}$	8.8
48*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Nb_{0.5}$	9.1
49*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Mo_{0.5}$	9.3
50*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Hf_{0.5}$	9.0
51*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}Ta_{0.5}$	9.4
52*	$Nd_{12}Fe_{71}Co_{10}B_{6.5}W_{0.5}$	8.7
53*	$Nd_{12}Fe_{72}Co_{10}B_6$	8.3

\*比較例

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